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FIELD	GROUP	SUB GR

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number): Polynitro "cage" compounds; Synthesis

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The synthesis and chemistry of novel polynitropolycyclic "cage" systems has been pursued in systematic fashion. The following new polynitropolycyclic compounds have been synthesized in the course of these studies: (i) 6,6,8-trinitropentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (**1**, a trinitro-1,3-bishomocubane), (ii) 6,6,10,10-tetranitropentacyclo[5.3.0.0^{2},5.0^{3},9.0^{4},8]decane (**2**, a tetranitro-1,3-bishomocubane), (iii) a series of nitro-substituted 2,3,4,8-tetraphenylpentacyclo[5.3.0.0^{2},5.0^{3},9.0^{4};8]decanes containing two, three, and four NO_2 groups, respectively, (iv) 8,8,11,11-tetranitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**3**, a tetranitropentacycloundecane), and (v) 4,4,7,7,11,11-hexanitropentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**4**, D_3-hexanitrotrishomocubane). The structures of compounds **1**, **2**, and **3** each have been obtained via single crystal X-ray structural analysis. The thermal behavior and detonation properties of D_3-hexanitrotrishomocubane (**4**) have been studied.

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SECURITY CLASSIFICATION OF THIS PAGE

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AFOSR-TR- 88-0915

FINAL TECHNICAL REPORT

SYNTHESIS OF NEW POLYNITROPOLYHEDRANES

AFOSR GRANT NO. AFOSR-84-0085

PERIOD COVERED: 1 APRIL 1984 - 31 MARCH 1988

Principal Investigator: Dr. Alan P. Marchand

Department of Chemistry, University of North Texas, Denton, TX 76203-5068

Alan P. Marchand

7 July 1988

TABLE OF CONTENTS

		Page
I.	Summary of Research Accomplishments	1
II.	Research Objectives	2
III.	Summary of Progress, FY84-88.	3
IV.	List of Publications (FY84-88) Acknowledging AFOSR Support.	17
V.	List of Professional Personnel Associated with the Grant .	23
VI.	Research Presentations	24

I. SUMMARY OF RESEARCH ACCOMPLISHMENTS

The synthesis and chemistry of novel polynitropolycyclic "cage" systems has been pursued in systematic fashion. The following new polynitropolycyclic compounds have been synthesized in the course of these studies: (i) 6,6,8-trinitropentacyclo-[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane (**1**, a trinitro-1,3-bishomocubane), (ii) 6,6,10,10-tetranitropentacyclo-[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane (**2**, a tetranitro-1,3-bishomocubane), (iii) a series of nitro-substituted 2,3,4,8-tetraphenylpentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decanes containing two, three, and four NO_2 groups, respectively, (iv) 8,8,11,11-tetranitropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**3**, a tetranitropentacycloundecane), and (v) 4,4,7,7,11,11-hexanitropentacyclo-[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**4**, D_3-hexanitrotrishomocubane). The structures of compounds **1**, **2**, and **3** each have been obtained via single crystal X-ray structural analysis. The thermal behavior and detonation properties of D_3-hexanitrotrishomocubane (**4**) have been studied.

II. RESEARCH OBJECTIVES

A significant portion of our overall research program has been concerned with the synthesis and chemistry of novel, strained polycyclic "cage" hydrocarbon systems. The objective of our AFOSR-sponsored research program is to extend our earlier interests in the pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (PCUD) and pentacyclo[5.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane (1,3-bishomocubane) ring systems to include the syntheses of new polynitro derivatives of these molecules. We seek new ways to incorporate increasing numbers of NO_2 groups into novel cage molecules with the ultimate goal of synthesizing a fully pernitrated cage molecule, $C_n(NO_2)m$.

Our approach to these syntheses involves introducing increasing numbers of NO_2 groups into a given cage system by employing a logical progression of increasingly functionalized synthetic intermeidates. Thus, we are able to gauge the cumulative effects of increasing substitution (particularly NO_2 substitution) upon product stability and upon the relative ease of product-forming reactions in a gradual and orderly fashion. Importantly, such approaches represent entirely new synthetic methodology for incorporating large numbers of NO_2 substituents into novel, strained systems.

III. SUMMARY OF PROGRESS, FY84-88

As part of our research efforts to synthesize new polynitropolycyclic compounds, we have identified four target molecules/molecular systems whose structures are shown in Figure 1. Typical synthetic methodology that has been utilized in our laboratory in pursuit of these target molecules is shown in Figure 2. Here, the substituted polycyclic framework is first constructed via a combination of thermal and photochemical cycloadditions. The substituent groups (generally cage ketone carbonyl groups or pendant carboxylic ester, acid or phenyl functionalities) are converted subsequently into nitro groups.

By utilizing the general approach shown in Figure 2, we have completed the syntheses of a trinitro- and of a tetranitro-1,3-bishomocubane in thirteen and in ten stereocontrolled steps, respectively (see Figure 3).[1,2] In addition, we have synthesized D_3-trishomocubanetrione (Figure 4), and we have successfully converted this material into the corresponding D_3-hexanitrotrishomocubane (our third target molecule, Figure 5).[3] Also, we recently completed the syntheses of a tetraphenyltetranitro-1,3-bishomocubane (Figure 6)[4] and of 8,8,11,11-tetranitropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$,$0^{5,9}$]undecane (a member of our second target molecular system, Figure 7).[5]

The thermal behavior and detonation properties of D_3-hexanitrotrishomocubane have been studied.[6] The DSC thermogram of this compound reveals the following characteristics: When a 3.34 mg sample was heated at 10 $^{o}C\text{-}min^{-1}$, exotherm onset occurred

at 272 ^{o}C, reached a maximum at 308 ^{o}C, and subsided at 331 ^{o}C. A second smaller exotherm was initiated at 331 ^{o}C, reached a maximum at 338 ^{o}C, and subsided at 355 ^{o}C. A study of the shock sensitivity of this compound as measured by the exploding foil slapper technique revealed that it is less shock-sensitive than TNT. Explosive output calculations reveal that D_3-hexanitrotrishomocubane is a substantially more powerful explosive than is TNT.[6]

Progress has accrued toward achieving the synthesis of our final target molecular system. We recently reported our synthesis of the corresponding heptacyclotetradecanedione, (Figure 8).[7] Conversion of each ketone functionality into geminal dinitro groups should be straightforward. In addition, we have made progress toward the synthesis of more highly substituted heptacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{4,11}$.$0^{5,9}$.$0^{10,14}$]tetradecanes, as detailed below.

The thermal reaction of $Fe(CO)_5$ with 2,3-dicarbomethoxynorbornadiene was studied in the hope that the coresponding cage dimer could be synthesized. However, we were disapointed to find that this reaction afforded only the corresponding exo,trans,exo dimer ketone: no cage dimer was produced in this reaction (Figure 9). In view of this result, an attempt was made to modify the substitution pattern on the norbornadiene substrate in the hope that this might promote the desired cyclodimerization reaction. Thus, 2,3-bis(acetoxymethyl)norbornadiene was prepared (Figure 10).

Here, the electron withdrawing CO_2Me groups in 2,3-dicarbomethoxynorbornadiene have been replaced by electron donating CH_2OAc groups. However, the only product obtained via thermal reaction of the bis(acetoxymethyl)norbornadiene was a novel bis[diene-$Fe(CO)_3$] complex (Figure 11), the structure of which was confirmed via single crystal X-ray structural analysis.[8]

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2. A. P. Marchand and D. S. Reddy, J. Org. Chem., **49**, 4078 (1984).

3. A. P. Marchand, G. V. Madhava Sharma, G. S. Annapurna, and P. R. Pednekar, J. Org. Chem. **52**, 4784 (1987).

4. A. P. Marchand, G. S. Annapurna, V. Vidyasagar, J. L. Flippen-Anderson, R. Gilardi, C. George, and H. L. Ammon, J. Org. Chem. **52**, 4781 (1987).

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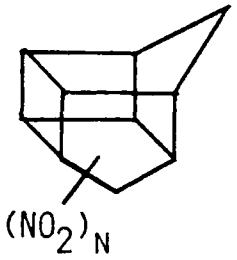
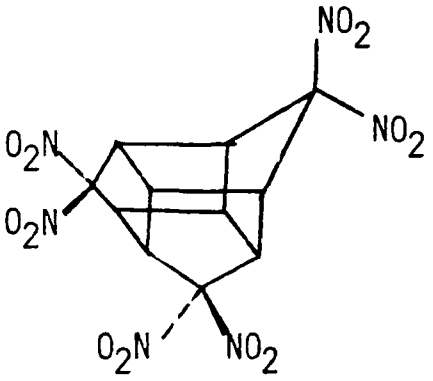
7. A. P. Marchand and A. D. Earlywine, J. Org. Chem., **49**, 1660 (1984).

8. W. H. Watson, A. Nagl, A. P. Marchand, and B. Chenera, Acta Cryst., Section C, **C44**, 806 (1988).

FIGURE 1. TARGET MOLECULES



(N = 3 - 8)



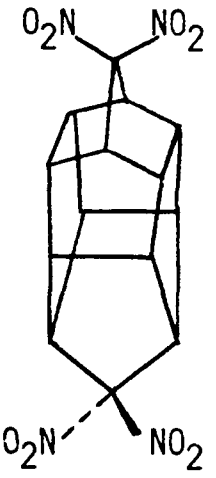
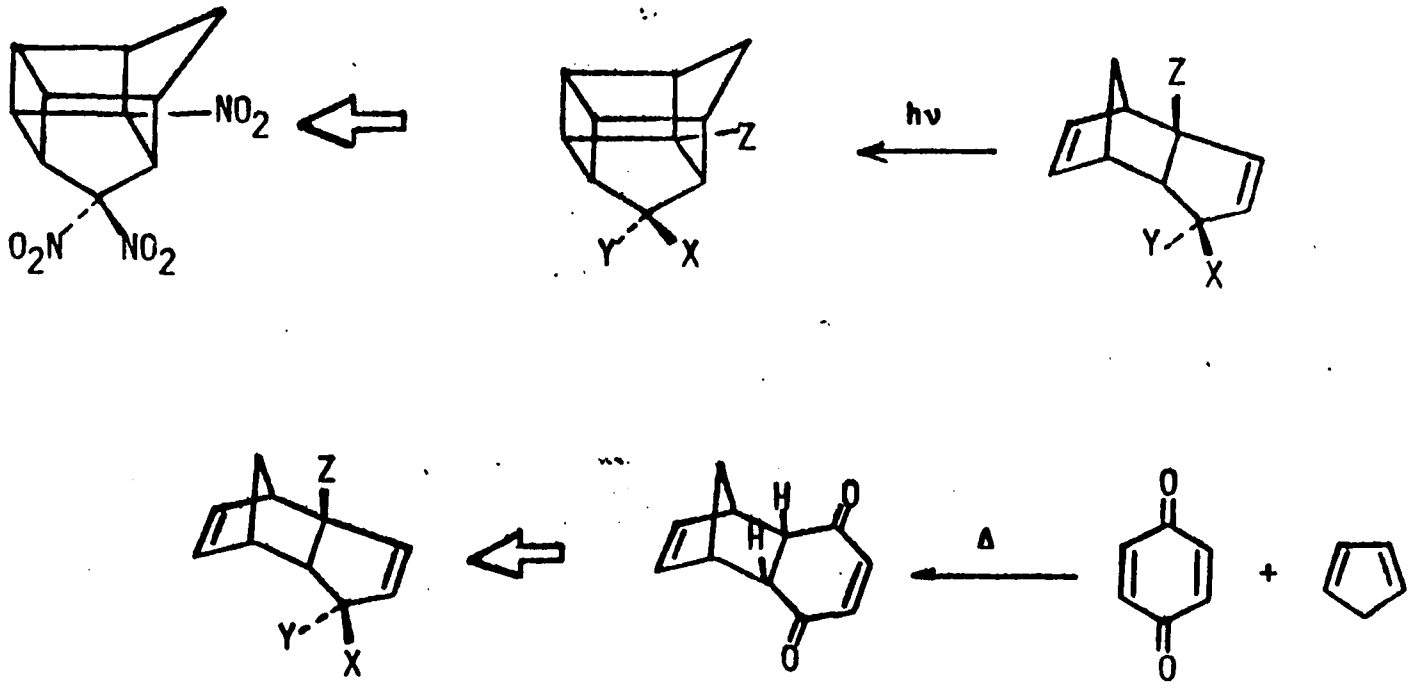


FIGURE 2

RETROSYNTHETIC PERSPECTIVE:



(X,Y = CARBONYL OXYGEN;
Z = CO_2ME)

REFERENCE: A. P. MARCHAND AND S. C. SURI, J. ORG. CHEM., 49, 2041 (1984).

FIGURE 3

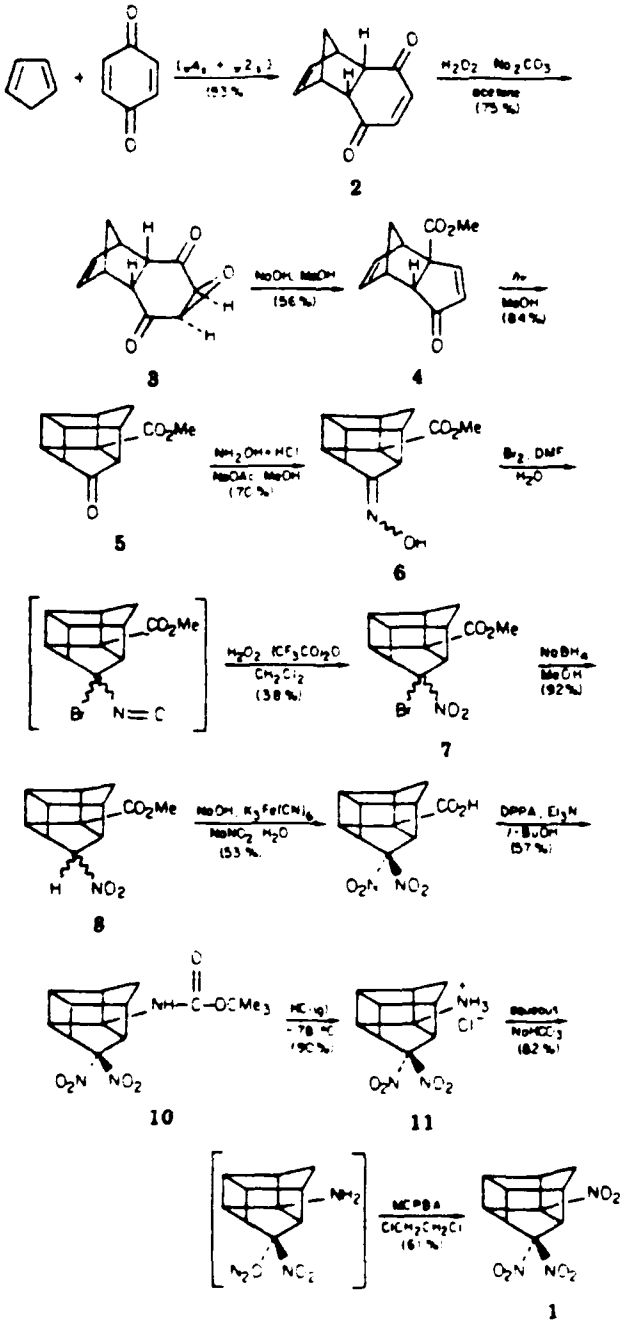
Synthesis of 3,5,5-Trinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane

Alan P. Marchand* and Suresh Chander Suri

Department of Chemistry, North Texas State University, Box 5068, Denton, Texas 76203

J. Org. Chem. 49, 2041-2043 (1984).

Scheme I



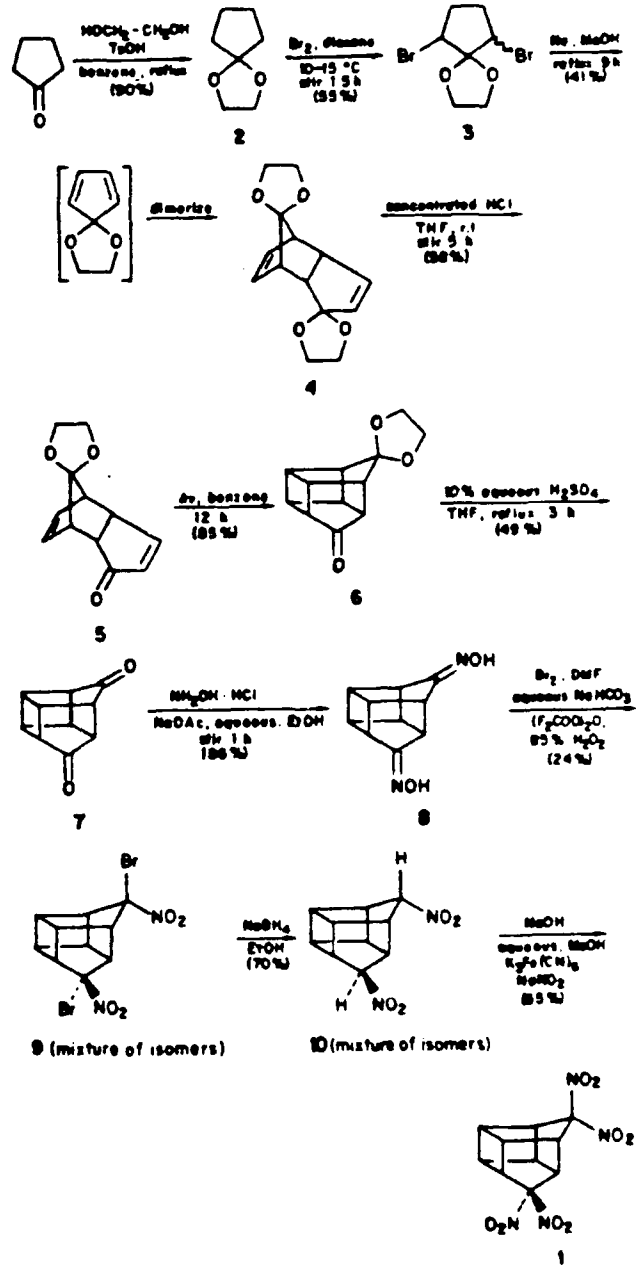
Synthesis of 5,5,9,9-Tetranitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane

Alan P. Marchand* and D. Sivakumar Reddy

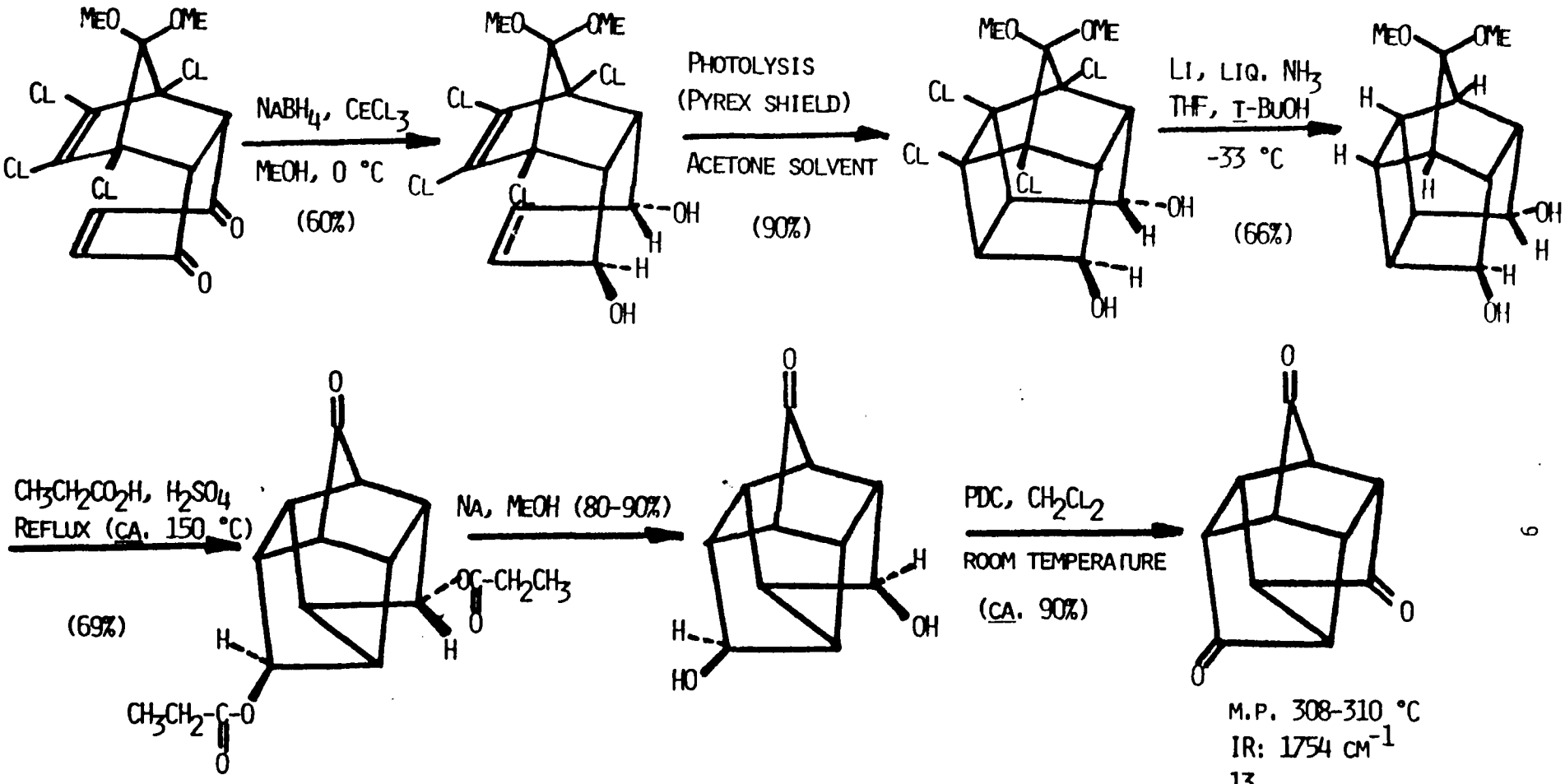
Department of Chemistry, North Texas State University, NTSU Station, Denton, Texas 76203

J. Org. Chem., 49, 4078-4080 (1984).

Scheme I



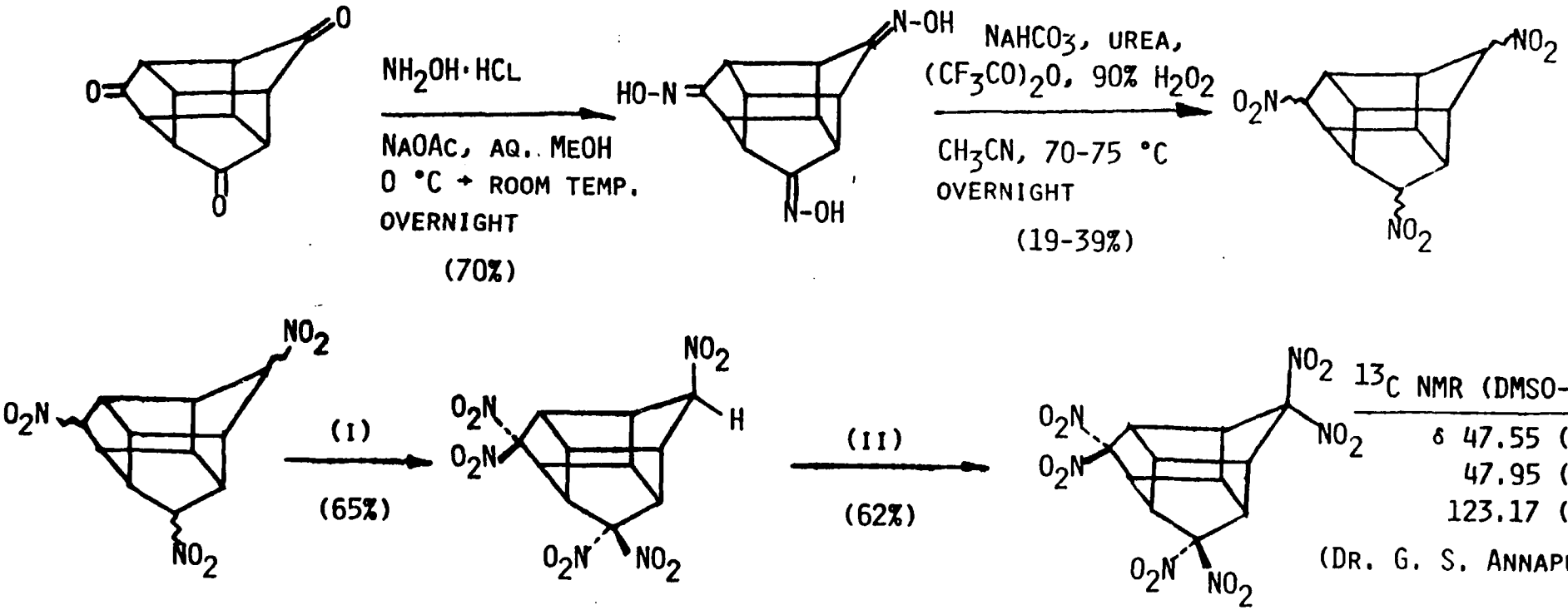
SYNTHESIS OF D_3-TRISHOMOCUBANETRIONE



M.P. 308-310 °C
IR: 1754 cm^{-1}
^{13}C NMR: 29.64 (D)
40.91 (D)
207.33 (S)

FIGURE 4

FIGURE 5



^{13}C NMR (DMSO-D_6)

δ 47.55 (D)
47.95 (D)
123.17 (S)

(DR. G. S. ANNAPURNA)

(I) (A) NAOH, AQ. MEOH (3 HR); (B) $K_3Fe(CN)_6$, AQ. $NaNO_2$, Et_2O (1 HR).

(II) (A) NAOH, AQ. MEOH (24 HR); (B) $K_3Fe(CN)_6$, AQ. $NaNO_2$, Et_2O (12 HR).

REFERENCE: N. KORNBLUM, H. K. SINGH, AND W. J. KELLY, J. ORG. CHEM., 48, 332 (1983).

Synthesis of Nitro Substituted 2,3,4,5-Tetraphenylpentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decanes

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Department of Chemistry, North Texas State University, Denton, Texas 76203-5068

Judith L. Flippen-Anderson,* Richard Gilardi, and Clifford George

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375

Herman L. Ammon*

Department of Chemistry, University of Maryland, College Park, Maryland 20742

Received March 24, 1987

There is considerable current interest in the synthesis and chemistry of energetic polycyclic "cage" compounds.[1-5] The title compounds are novel, strained energetic materials that have been prepared as part of an ongoing program involved with the synthesis of new polynitro-1,3-bishomocubanes. Two such systems, a trinitro- and a tetranitro-1,3-bishomocubane (**1**[3] and **2**[4], respectively) have been prepared in our laboratory, and their respective structures have been determined via single-crystal X-ray crystallography.[6,7]

Three compounds, a dinitro- (**3**), a trinitro- (**4**), and a tetranitro-2,3,4,8-tetraphenylpentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (**5**), have been prepared in the present study.

(1) Sollott, G. P.; Gilbert, E. E. *J. Org. Chem.* **1980**, *45*, 5405.
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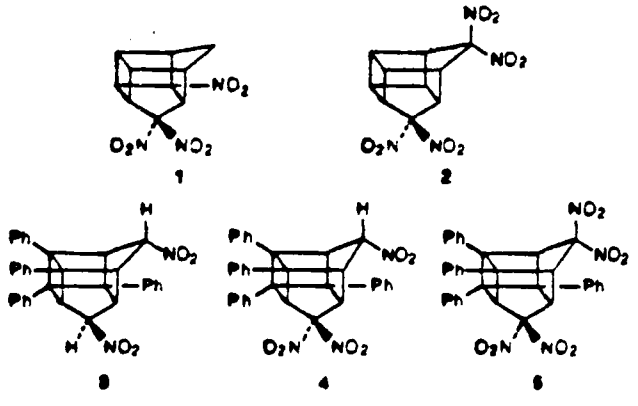
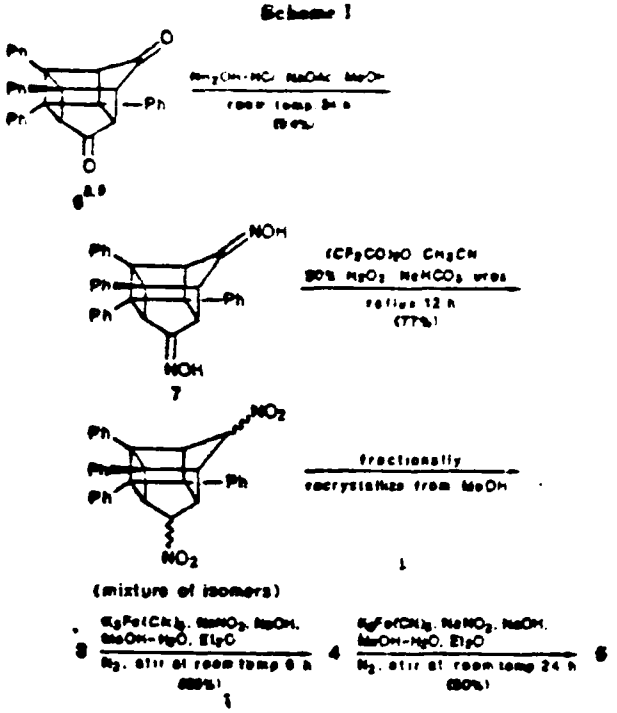
(3) Marchand, A. P.; Suri, S. C. *J. Org. Chem.* **1984**, *49*, 2041.
(4) Marchand, A. P.; Reddy, D. S. *J. Org. Chem.* **1984**, *49*, 4078.
(5) Paquette, L. A.; Fischer, J. W.; Engel, P. *J. Org. Chem.* **1985**, *50*, 2524.
(6) Ammon, H. L.; Zhang, D.; Choi, C. S.; Sandus, O.; Marchand, A. P.; Suri, S. C. *Acta Crystallogr. Sect. C* **1985**, *C41*, 404.
(7) George, C.; Gilardi, R.; Flippen-Anderson, J. L.; Choi, C. S.; Marchand, A. P.; Reddy, D. S. *Acta Crystallogr., Sect. C* **1985**, *C41*, 788.

0022-3263/87/1952-4781$01.50/0



Scheme I



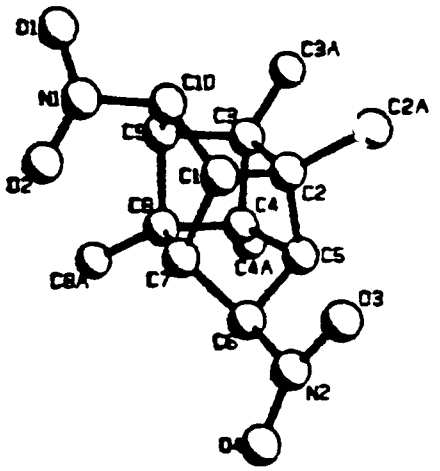


Figure 1. Results of the X-ray study on **3**. For clarity, the phenyl groups on C-2, C-3, C-4, and C-8 are represented as single atoms (C-2a, C-3a, C-4a, and C-8a).

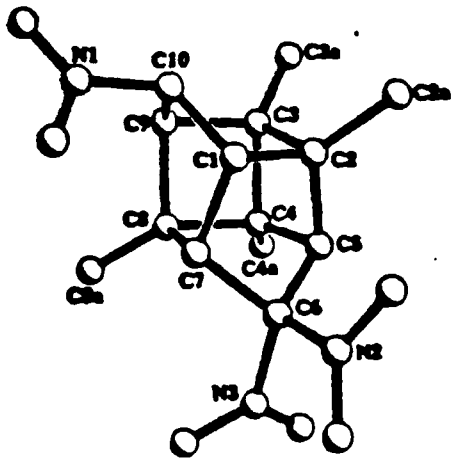
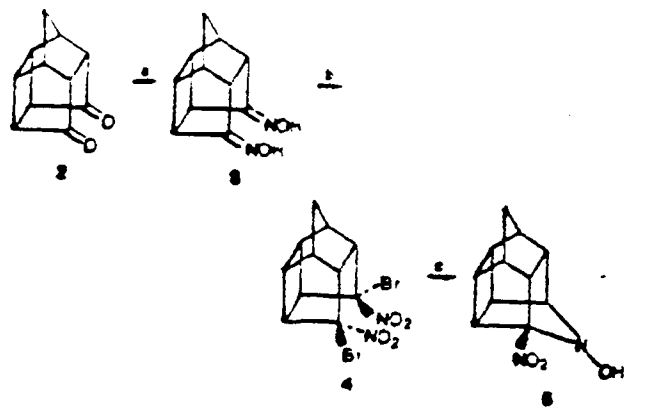


Figure 2. Results of the X-ray study on **4**. For clarity, the phenyl groups on C-2, C-3, C-4, and C-8 are represented as single atoms (C-2a, C-3a, C-4a, and C-8a).

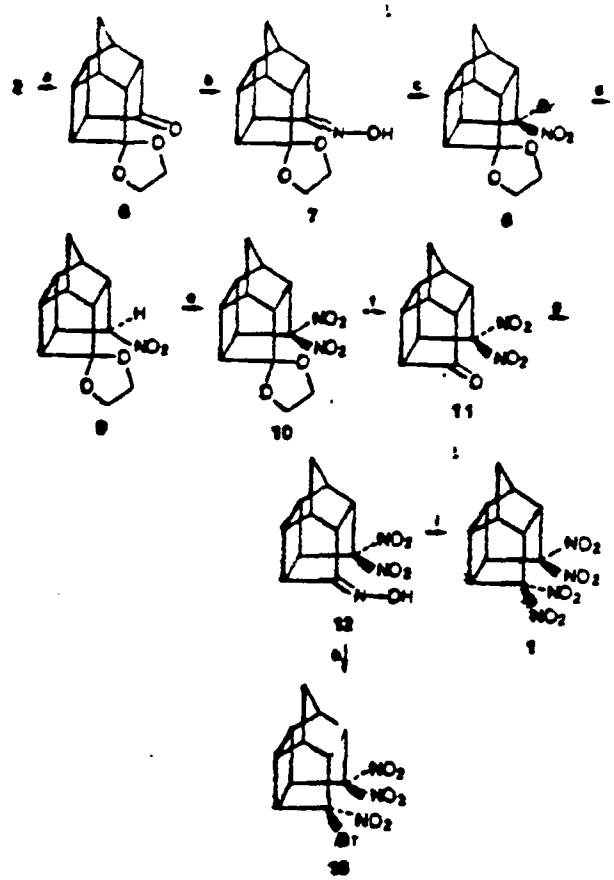
A. P. MARCHAND, B. E. ARNEY, JR., AND P. R. DAVE, J. ORG. CHEM. 53, 443 (1988).

Scheme I*



*(a) $NH_2OH \cdot HCl$, NaOAc, EtOH (87%); (b) NBS, $NaHCO_3$, dioxane, room temperature, 48 h (49%); (c) $NaBH_4$, 60% aqueous EtOH, room temperature, 45 min (28%).

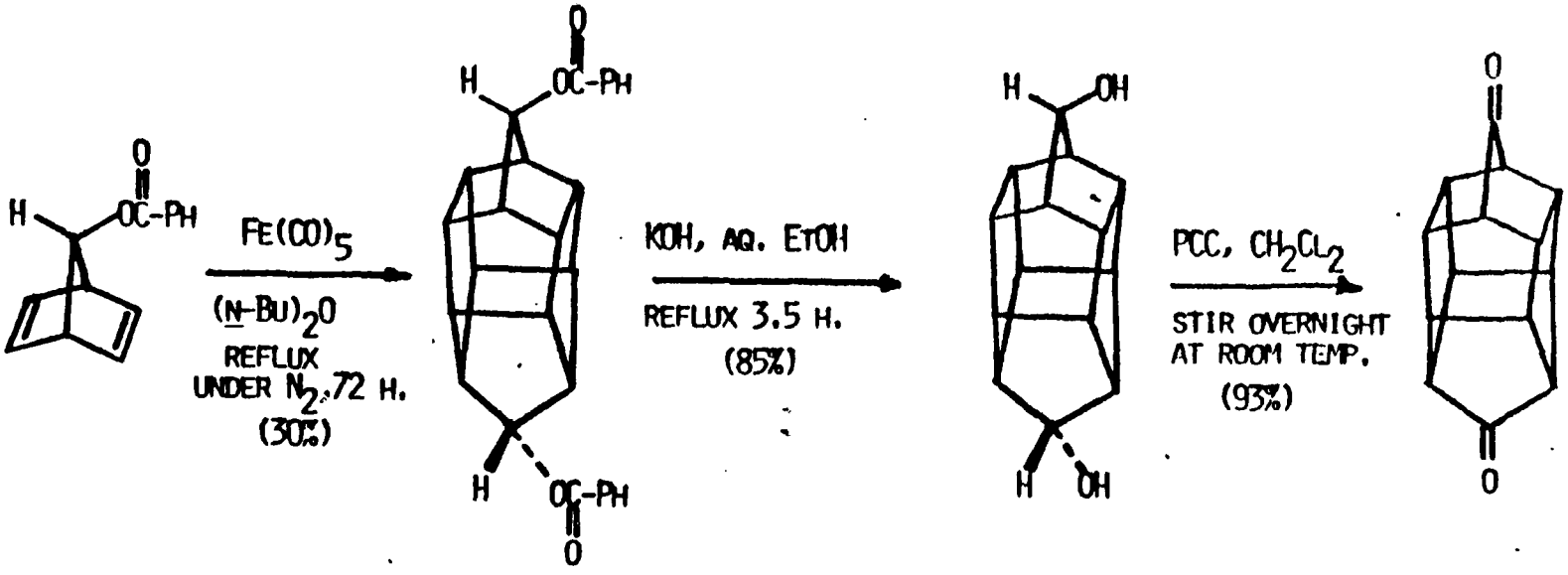
Scheme II*



*(a) $HOCH_2CH_2OH$, TsOH, benzene, Dean–Stark tube (92%); (b) $NH_2OH \cdot HCl$, NaOAc, EtOH, room temperature, overnight (79%); (c) Br_2, $NaHCO_3$, DMF, 0 °C, and then O_3, CH_2Cl_2, 0 °C (80%); (d) $NaBH_4$, 60% aqueous EtOH, room temperature, 0.5 h (97%); (e) $K_3Fe(CN)_6$, $NaNO_2$, aqueous MeOH, NaOH, room temperature, 0.5 h (73%); (f) concentrated H_2SO_4, CH_2Cl_2, room temperature, overnight (73%); (g) $NH_2OH \cdot HCl$, NaOAc, EtOH, room temperature, overnight (89%); (h) NBS, $NaHCO_3$, 5% aqueous dioxane, room temperature, 72 h (65.7%); (i) 98% red HNO_3, NH_4NO_3, CH_2Cl_2, reflux 1 h, then 30% H_2O_2, reflux 1 h (31%, 64% based on recovered 11).

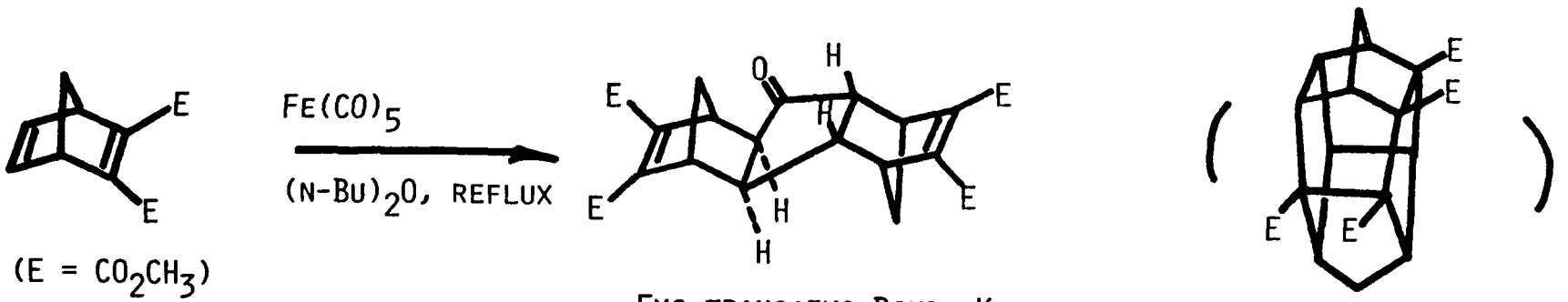
FIGURE 7

FIGURE 8



REFERENCE: A. P. MARCHAND AND A. D. EARLYWINE, J. ORG. CHEM., 49, 1660 (1984).

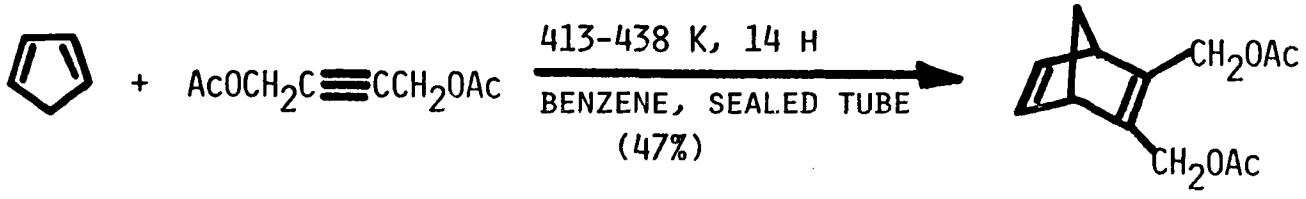
FIGURE 9

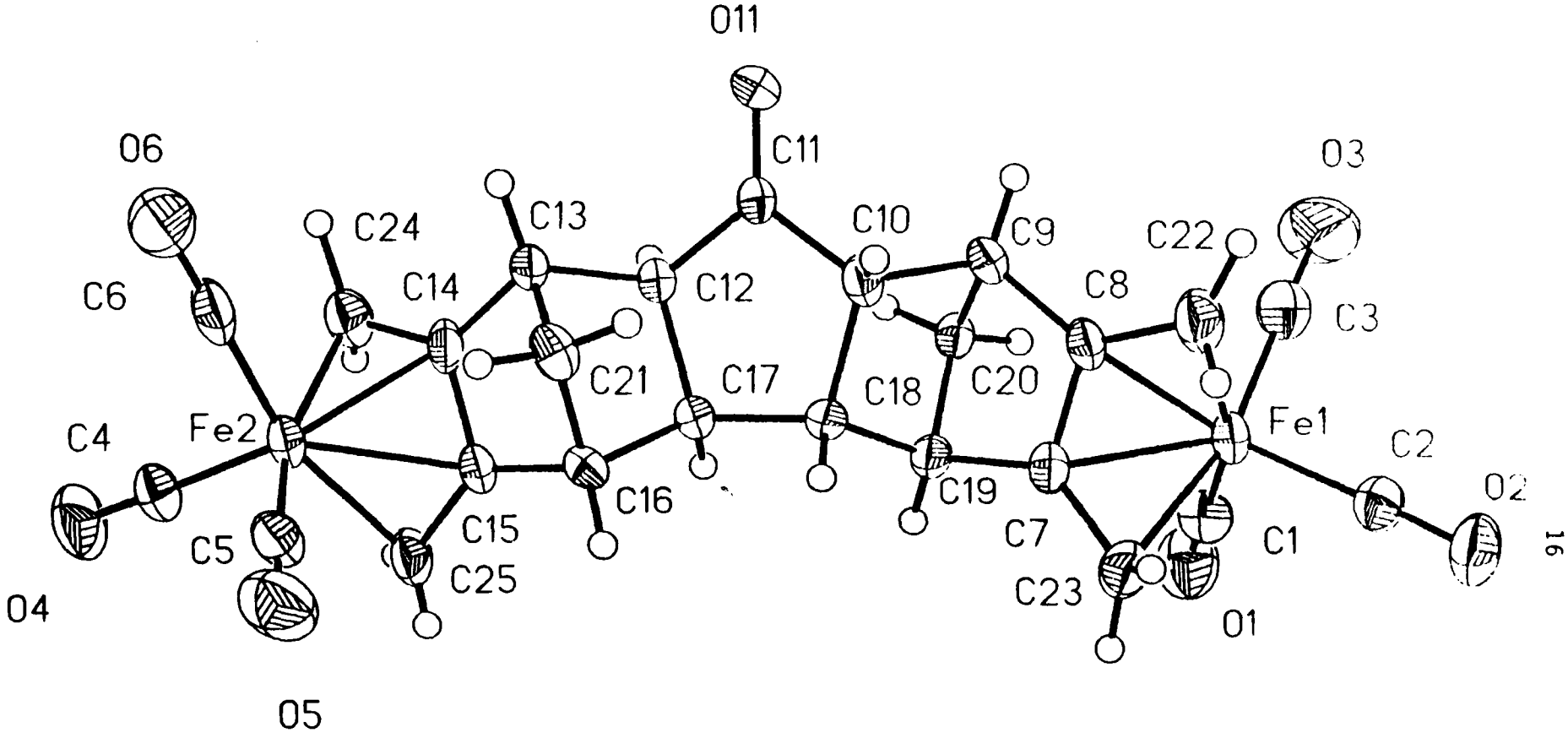


EXO,TRANS;EXO DIMER KETONE
(ONLY THIS PRODUCT COULD BE ISOLATED FROM THE REACTION MIXTURE)

(NOT FOUND)

FIGURE 10


+ AcOCH2C≡CCH2OAc
413-438 K, 14 H
BENZENE, SEALED TUBE
(47%)
CH2OAc
CH2OAc


O11
C11
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C9
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C6
C14
C12
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C3
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C18
C20
C4
Fe2
Fe1
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C16
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C23
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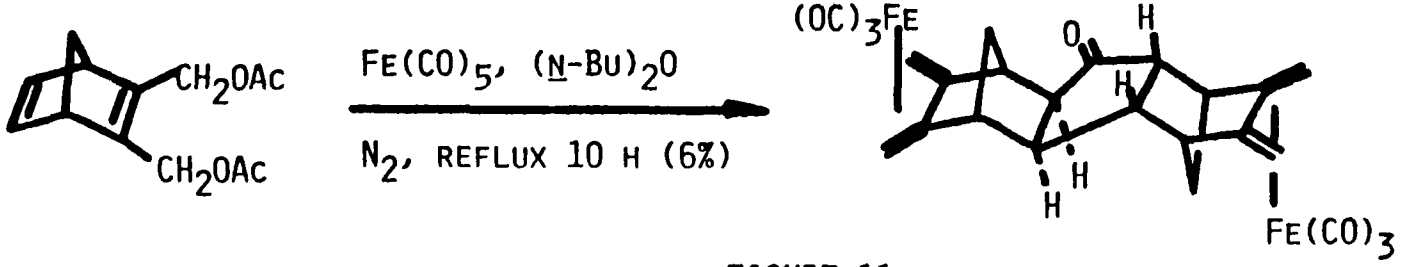
CH2OAc
CH2OAc
Fe(CO)5, (N-Bu)2O
N2, REFLUX 10 H (6%)
(OC)3Fe
O
H
H
H
H
Fe(CO)3

FIGURE 11

IV. LIST OF PUBLICATIONS (FY84-88) ACKNOWLEDGING AFOSR SUPPORT

DR. ALAN P. MARCHAND: GRANT NO. AFOSR-84-0085

1. Alan P. Marchand and Arthur D. Earlywine, "Heptacyclo-[5.5.1.1^{4,10}.0^{2,6}.0^{3,11}.0^{5,9}.0^{8,12}]tetradecane-13,14-dione: A Novel, Polycyclic Perpendobiplanar D_{2d} Diketone", J. Org. Chem., 49, 1660-1661 (1984).

2. Alan P. Marchand and Suresh C. Suri, "Synthesis of 3,5,5-Trinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane", J. Org. Chem., 49, 2041-2043 (1984).

3. Alan P. Marchand, David B. Goodin, M. B. Hossain, and D. van der Helm, "On the Stereochemistry of the Reaction of 7-Substituted Norbornadienes with Iron Carbonyls. II. Reaction of Iron Pentacarbonyl with 7-Phenyl- and 7-ortho-Anisylnorbornadiene", with D. B. Goodin, M. B. Hossain, and D. van der Helm, J. Org. Chem., 49, 2897-2900 (1984).

4. Goverdhan Mehta, K. Sambasiva Rao, Alan P. Marchand, and R. Kaya, "Studies on the Flash Vacuum Pyrolysis and Anomalous Course of Alkali Metal Promoted Reductions of 8-Methylenepentacyclo-[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-11-one", J. Org. Chem., 49, 3848-3852 (1984).

5. Alan P. Marchand and D. Sivakumar Reddy, "Synthesis of 5,5,9,9-Tetranitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane", J. Org. Chem., 49, 4078-4080 (1984).

6. Alan P. Marchand and An-hsiang Wu, "Heptacyclo-[5.5.1.1^{4,10}.0^{2,6}.0^{3,11}.0^{5,9}.0^{8,12}]tetradecane-13,14-bis(spiro-1'-cyclopentane): A New $C_{22}H_{28}$ Nonacyclic Cage

Hydrocarbon. Improved Synthesis of Bicyclo[2.2.1]hepta-2,5-diene- 7-spiro-1'-cyclopentane", J. Org. Chem., 50, 396-398 (1985).

7. Alan P. Marchand and D. Sivakumar Reddy, "Base-Promoted Rearrangement of Cage Alpha-Haloketones. 3. 3,6-Dibromo-tetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undecane 2,7-dione", J. Org. Chem., 50, 724-725 (1985).

8. Herman L. Ammon, Chang S. Choi, Oscar Sandus, Alan P. Marchand, and Suresh C. Suri, "3,5,5-Trinitropentacyclo-[5.3.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]decane, $C_{10}H_9(NO_3)_2$", Acta Cryst. Section C, 41C, 404-406 (1985).

9. Clifford George, Richard Gilardi, Judith L. Flippen-Anderson, Chang S. Choi, Alan P. Marchand, and D. Sivakumar Reddy, "5,5,9,9-Tetranitropentacyclo[5.3.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]decane", Acta Cryst., Section C, 41C, 788-791 (1985).

10. Istvan Hargittai, J. Brunvoll, S. J. Cyvin, and Alan P. Marchand, "The Molecular Geometry of a Heptacyclotetradecane from Gas-Phase Electron Diffraction", J. Mol. Struct., **140**, 219-225 (1986).

11. Alan P. Marchand, Riza Kaya, S. W. Muchmore, and D. van der Helm, "Formation of Sulfonium Tetrafluoroborates from Reactions of γ,δ-Unsaturated Ketones with Thiols in the Presence of Boron Trifluoride Etherate", J. Org. Chem., **51**, 1622-1625 (1986).

12. Alan P. Marchand, William D. LaRoe, G. V. Mahdava Sharma, Suresh C. Suri, and D. Sivakumar Reddy, "Facile Stereoselective Reductions of Enediones and Cage Diketones Using $NaBH_4$-$CeCl_3$", J.

Org. Chem., **51**, 1622-1625 (1986).

13. Alan P. Marchand and An-hsiang Wu, "Synthesis of New Substituted Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecanes: A Novel Synthesis of Hexacyclo[6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$.$0^{5,9}$]-dodecane (1,3-Bishomopentaprismane)", J. Org. Chem., **51**, 1897-1900 (1986).

14. William B. Smith, Alan P. Marchand, Suresh C. Suri, and Pei-wen Jin, "Synthesis of the Two Epimeric 2-Carbomethoxy-3,7-dimethyl-endo-tricyclo[5.2.1.$0^{2,6}$]dec-8-en-5-ones. Unequivocal Structural Assignment of the 5 - and 5 -Isomers via 2D NMR Spectroscopy", J. Org. Chem., **51**, 3052-3054 (1986).

15. Alan P. Marchand, Arthur D. Earlywine, and Mary Jane Heeg, "Stereochemistry of the Reaction of 7-Substituted Norbornadienes with Iron Carbonyls. 3. Reaction of $Fe(CO)_5$ with 7-(Benzoyloxy)norbornadiene", J. Org. Chem., **51**, 4096-4100 (1986).

16. William T. Brady, Y. F. Giang, Alan P. Marchand, and An-hsiang Wu, "A New Preparation of Ketenes for Intramolecular Cycloadditions", Synthesis, 395-396 (1987).

17. William H. Watson, Iraj Tavanaiepour, Alan P. Marchand, and Paritosh R. Dave, "3-(p-Cyanophenoxy)quadricyclane", Acta Cryst., Section C, **C43**, 1356-1359 (1987).

18. William H. Watson, Alan P. Marchand, and Paritosh R. Dave, "Structure of a Novel $C_{11}H_{12}N_2O_3$ Cage Molecule", Acta Cryst., Section C, **C43**, 1569-1571 (1987).

19. William T. Brady, Yun-sen Frank Giang, Alan P. Marchand, and An-hsiang Wu, "Intramolecular [2 + 2] Cycloadditions of Ketenes to

Carbonyl Groups. A Novel Synthesis of Substituted Benzofurans", J. Org. Chem., **52**, 3457-3461 (1987).

20. Judith L. Flippen-Anderson, Richard Gilardi, Clifford George, Alan P. Marchand, and Pei-wen Jin, "1,6-Dimethyl-1α,4α,4aα,5α,8β,8aα-hexaydro-1,4-methanonaphthalene-5,8-diol, $C_{13}H_{18}O_2$", Acta Cryst., Section C, **C43**, 2151-2153 (1987).

21. Alan P. Marchand, Benny E. Arney, Jr., Richard Gilardi, and Judith L. Flippen-Anderson, "Lewis Acid-Promoted Reaction of Pentacyclo[5.4.0.,$0^{2,6}.0^{3,10}.0^{5,9}$]undecane-8.11-dione: A Synthetic Entry into the Pentacyclo[6.5.0.$0^{4,12}.0^{5,10}.0^{9,13}$]-tridecane Ring System", J. Org. Chem., **52**, 3455-3457 (1987).

22. Judith L. Flippen-Anderson, Richard Gilardi, Clifford George, Alan P. Marchand, and Arthur D. Earlywine, "syn-8,syn-13-Bis(benzoyloxy)heptacyclo-[7.6.0.$0^{2,7}.0^{4,14}.0^{5,12}.0^{6,10}.0^{11,15}$]pentadecan-3-one, $C_{29}H_{24}O_5$", Acta Cryst., Section C, **C43**, 2364-2366 (1987).

23. Alan P. Marchand, G. S. Annapurna, V. Vidyasagar, Judith L. Flippen-Anderson, Richard Gilardi, Clifford George, and Herman L. Ammon, "Synthesis of Nitro-Substituted 2,3,4,8-Tetraphenyl-pentacyclo[5.3.0.$0^{2,5}.0^{3,9}.0^{4,8}$]decanes", J. Org. Chem., **52**, 4781-4783 (1987).

24. Alan P. Marchand, G. V. Madhava Sharma, G. S. Annapurna, and Purushottam R. Pednekar, "Syntheses of Pentacyclo-[5.4.0.$0^{2,6}.0^{3,10}.0^{5,9}$]undecane-4,8,11-trione, Pentacyclo-[6.3.0.$0^{2,6}.0^{3,10}.0^{5,9}$]undecane-4,7,11-trione (D_3-Trishomocubanetrione) and 4,4,7,7,11,11-Hexanitro-

pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (D_3-Hexanitrotrishomocubane)", J. Org. Chem., **52**, 4784-4788 (1987).

25. Alan P. Marchand, Pei-wen Jin, Judith L. Flippen-Anderson, Richard Gilardi, and Clifford George, "A Novel Rearrangement in the 1,3-Bishomocubyl Ring System", J. Chem. Soc., Chem. Commun., 1108-1109 (1987).

26. Alan P. Marchand, Chunmin Huang, Riza Kaya, A. David Baker, E. D. Jemmis, and David A. Dixon, "Photoelectron Spectra and Electronic Structures of Substituted Pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecanes", J. Am. Chem. Soc. **109**, 7095-7101 (1987).

27. Alan P. Marchand, Benny E. Arney, Jr., and Paritosh R. Dave, "Synthesis of 8,8,11,11-Tetranitropentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane", J. Org. Chem., **53**, 443-446 (1988).

28. Alan P. Marchand, "Synthesis and Chemistry of Novel Polynitropolycyclic Cage Molecules" (Tetrahedron Reports No. 233), Tetrahedron **44**, 2377-2395 (1988).

29. Alan P. Marchand, Paritosh R. Dave, N. Satyanarayana, and Benny E. Arney, Jr., "Reductive Amination of Pentacyclo-[5.4.0.$0^{2.6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione", J. Org. Chem., **53**, 1088-1092 (1988).

30. William H. Watson, Ante Nagl, Alan P. Marchand, and Balan Chenera, "Structure of a Bis(η^4-exocyclic-1,3-diene)Fe$(CO)_3$ Complex", Acta Cryst., Section C, **C44**, 806-808 (1988).

31. William H. Watson, Alan P. Marchand, and Paritosh R. Dave, "A Dimer Ketone Formed via $Fe(CO)_5$-Promoted Coupling of 7-Phenoxynorbornadiene to Carbon Monoxide", Acta Cryst., Section C, **C44**, 940-942 (1988).

32. Alan P. Marchand, Benny E. Arney, Jr., Paritosh R. Dave, N. Satayanarayana, William H. Watson, and Ante Nagl, "Transannular Cyclizations in the Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]-undecane-8,11-dione System: A Reinvestigation", J. Org. Chem., **53**, 2644-2647 (1988).

33. Gary S. Linz, Andrew S. Zektzer, Gary E. Martin, Alan P. Marchand, and Pei-wen Jin, "Structural Assignment of a Methylcyclopentadiene-Toluquinone Diels-Alder Cycloadduct. Analysis of the 2D-NMR Spectrum of 1,6-Dimethyl-1α,4α,4aα,5α,8β,8aα-hexahydro-1,4-methanonaphthalene-5,8-diol", J. Org. Chem., **53**, 2647-2650 (1988).

34. Judith L. Flippen-Anderson, Richard Gilardi, Clifford George, Alan P. Marchand, Pei-wen Jin, and Mahendra N. Deshpande, "Structure of a Novel $C_{22}H_{24}$ Cage Dimer", Acta Cryst., Section C, in press (1988).

35. Alan P. Marchand, "Molecules of Theoretical Interest: The Chemistry of Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (PCUD) and Related Systems", (a review with 83 references) in R. P. Thummel (Editor), "Advances in Theoretically Interesting Molecules", JAI Press, Inc., Greenwich, CT, Volume 1, in press (1988).

V. LIST OF PROFESSIONAL PERSONNEL ASSOCIATED WITH GRANT NO. AFOSR-84-0085

1984-1988

I. Undergraduate Research Assistants

A. Ms. Monique Davenport (1984)

II. Graduate Research Assistants

A. Mr. William LaRoe (1984; M. S., 1986)

B. Mr. Dalian Zhao (1987; M. S. expected, December, 1988)

III. Postdoctoral Research Associates

A. Dr. Sanjay Basak (1984-85)

B. Dr. Balan Chenera (1986-87)

C. Dr. Paritosh Dave (1987-88)

D. Dr. Mahendra Deshpande (1987-88)

E. Dr. Ben-min Gong (1986)

F. Dr. D. Rajapaksa (1988)

G. Dr. G. Madhusudhan Reddy (1987-88)

H. Dr. S. Pulla Reddy (1987-88)

I. Dr. D. Sivakumar Reddy (1984-85)

J. Dr. G. V. Madhava Sharma (1985)

K. Dr. V. Vidyasagar (1987-88)

VI. RESEARCH PRESENTATIONS, APRIL 1, 1984 - MARCH 31, 1988

DR. ALAN P. MARCHAND: AFOSR-84-0075

1. A. P. Marchand and P.-W. Jin, "An Approach to the Synthesis of 2,4,5,5-Tetranitropentacyclo[5.3.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]decane", Dallas-Ft. Worth Section of the American Chemical Society, Meeting-in-Miniature, Department of Chemistry, University of Texas at Dallas, Richardson, TX, April 27, 1984, (Contributed).

2. A. P. Marchand and A.-H. Wu, "Synthesis of a New Nonacyclic $C_{22}H_{28}$ Cage Hydrocarbon System", Dallas-Ft. Worth Section of the American Chemical Society, Meeting-in-Miniature, Department of Chemistry, University of Texas at Dallas, Richardson, TX, April 27, 1984, (Contributed).

3. A. P. Marchand, S. C. Suri, D. S. K. Reddy and P. R. Pednekar, "Synthesis of New Polynitropolycyclic Systems", Working Group Meeting on the Synthesis of High Density Energetic Materials, U. S. Army AMCCOM, Picatinny Arsenal, Dover, New Jersey, May 22-24, 1984, (Invited; I was co-organizer of this meeting with Dr. Jack Alster and Dr. Sury Iyer).

4. A. P. Marchand, "Stereochemistry and Mechanism of the Iron Carbonyl-Promoted Coupling of Strained Alkenes to Carbon Monoxide", A.T.& T. Bell Laboratories, Murray Hill, NJ, June 29, 1984, (Invited).

5. A. P. Marchand, "High Energy/High Density Polycyclic Hydrocarbons: Potential New Fuels for Air-Breathing Missiles", U. S. Army AMCCOM, Picatinny Arsenal, Dover, New Jersey, July 9, 1984, (Invited).

6. A. P. Marchand, "High Energy/High Density Polycyclic Hydrocarbons: Potential New Fuels for Air-Breathing Missiles", Naval Air Systems Command Program Review (held at North Texas State University), August 22, 1984, (Invited: I organized this meeting).

7. S. C. Suri and A. P. Marchand, "A New Approach to the Synthesis of Silphinene. A New and Potentially General Method for the Synthesis of Triquinanes", 188th National Meeting of the American Chemical Society, Philadelphia, PA, August 26-31, 1984, Paper No. ORGN 55, (Contributed).

8. A. P. Marchand, "High Energy/High Density Polycyclic Hydrocarbons: Potential New Fuels for Air-Breathing Missiles", Naval Air Systems Command Program Review (held at NAVAIR Headquarters, Washington, D. C.), September 18, 1984, (Invited).

9. A. P. Marchand, "Stereochemistry and Mechanism of the Iron Carbonyl-Promoted Coupling of 7-Substituted Norbornadienes to Carbon Monoxide", Department of Chemistry, Southern Methodist University, Dallas, TX, October 3, 1984, (Invited).

10. A. P. Marchand, "Synthesis of Novel Polycyclic Hydrocarbon Systems", Texas Synthesis Conference, Winedale, Texas, November 3, 1984, (Invited).

11. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, Texas Christian University, Ft. Worth, TX, November 8, 1984, (Invited).

12. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, Rice University, Houston, TX, January 28, 1985, (Invited).

13. A. P. Marchand, S. C. Suri, and D. S. K. Reddy, "Synthesis of New Polynitropolyhedranes", Air Force Office of Scientific Research Program Review, 1985 AFOSR/AFRPL Rocket Propulsion Research Meeting, Lancaster, CA, March 18, 1985, (Invited).

14. Jinren Ko, W. T. Brady, D. Sivakumar Reddy, and A. P. Marchand, Cycloaddition of Dichloroketene to Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]-undecane-8,11-dione", American Chemical Society Meeting-in-Miniature, North Texas State University, April 19, 1985, Paper No. 40, (Contributed).

15. A. P. Marchand, William D. LaRoe, and S. C. Suri, "Facile Stereoselective Reductions of Enediones and Cage Diketones Using $NaBH_4$-$CeCl_3$. American Chemical Society Meeting-in-Miniature, North Texas State University, April 19, 1985, Paper No. 41, (Contributed).

16. A. P. Marchand, "Stereochemistry and Mechanism of the Iron Carbonyl-Promoted Coupling of 7-Substituted Norbornadienes to Carbon Monoxide", Department of Chemistry, Trinity University, San Antonio, TX, April 26, 1985, (Invited).

17. A. P. Marchand, R. Kaya, S W. Muchmore and D. van der Helm, "Formation of Sulfonium Tetrafluoroborates from Reactions of Gamma, Delta-Unsaturated Ketones with Thiols in the Presence of Boron Trifluoride Etherate", 189th National Meeting of the American Chemical Society, Miami Beach, FL, April 28-May 3, 1985, (Contributed).

18. A. P. Marchand, "Synthesis of New High Energy/High Density Polycyclic Hydrocarbons", Naval Air Systems Command Program Review, Wright Patterson Air Force Base, Dayton, Ohio, May 13, 1985, (Invited).

19. A. P. Marchand, "Synthesis of New Polynitropolyhedranes", Office of Naval Research Program Review, Arlington, Virginia, May 29, 1985, (Invited).

20. A. P. Marchand, S. C. Suri, P.-W. Jin, and D. S. Reddy, "Synthesis of New Polynitropolycyclic Systems", Fourth Annual Working Group Meeting on Synthesis of High Energy Density Materials, U. S. Army Armament Research and Development Center, Dover, New Jersey, June 5, 1985, (Invited).

21. A. P. Marchand, C. Huang, R. Kaya, A. D. Baker, and E. D. Jemmis, "Synthesis of Alkene-Substituted Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]-undecanes. Synthesis and Photoelectron Spectra of Substituted Pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecanes", Gordon Research Conference on Physical Organic Chemistry, Wolfeboro, NH, June 13, 1985, (Invited).

22. A. P. Marchand and S. C. Suri, "Stereocontrolled Synthesis of Silphinene", 15th Annual Northeast Regional Meeting of the American Chemical Society, State University of New York, New Paltz, NY, June 25, 1985, Paper No. 123, (Contributed).

23. A. P. Marchand, C. Huang, and R. Kaya, "Synthesis of Methylene-pentacycloundecanes via Alpha-Silylcarbanion Intermediates. Synthesis and Photoelectron Spectra of Substituted Pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecanes", 15th Annual Northeast Regional Meeting of the American Chemical Society, State University of New York, New Paltz, NY, June 26, 1985, Paper No. 133, (Contributed).

24. A. P. Marchand, "Synthesis of New Polynitropolycyclic Systems", Joint Technical Coordinating Group for Munitions Development, Working Party for Explosives, U. S. Army Armament Research and Development Center, Dover, NJ, July 30, 1985, (Invited).

25. W. T. Brady, A. P. Marchand, J. Ko, S. B. Williams, A.-H. Wu, and D. S. Reddy, "Cycloaddition of Dichlorketene to C=O and C=C Bonds in Substituted Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecanes", 190th National Meeting of the American Chemical Society, Chicago, IL, September 8-13, 1984, Paper No. 52, (Contributed).

26. A. P. Marchand, "Synthesis of New Polynitropolycyclic Compounds", Meeting of the Steering Committee, Improved Performance on Target (IPOT) Program, United States Army; meeting held at Department of Chemistry, University of Chicago, Chicago, IL, September 19, 1985, (Invited).

27. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, Texas Tech University, Lubbock, TX, October 2, 1985, (Invited).

28. A. P. Marchand, "Synthesis of Natural and Unnatural Products",

Department of Medicinal Chemistry and Pharmacognosy, The University of Houston, Houston, TX, January 22, 1986, (Invited).

29. A. P. Marchand, "Synthesis of Suitable Precursors to Novel Polynitropolycyclic Compounds", Program Review and Meeting of the Steering Committee, U. S. Army's Improved Performance on Target (IPOT) Program, Department of Chemistry, The University of New Orleans, New Orleans, LA, January 23, 1986, (Invited).

30. A. P. Marchand, "Applications of Mass Spectrometry to Problems in Organic Chemistry", Department of Chemistry, Texas Lutheran College, Seguin, TX, February 11, 1986, (Invited).

31. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, The University of Texas at San Antonio, San Antonio, TX, February 12, 1986, (Invited).

32. A. P. Marchand, "Synthesis of New Polynitropolycyclic Compounds" Los Alamos National Laboratory, Los Alamos, NM, March 11, 1986 (Invited).

33. A. P. Marchand, "Stereochemistry and Mechanism of the Iron Carbonyl-Promoted Coupling of 7-Substituted Norbornadienes to Carbon Monoxide", Los Alamos National Laboratory, Los Alamos, NM, March 12, 1986 (Invited).

34. A. P. Marchand, A. D. Earlywine, and M. J. Heeg, "Iron Carbonyl-Promoted Coupling of 7-Benzoyloxynorbornadiene to Carbon Monoxide", 191st National Meeting of the American Chemical Society, New York, NY, April 15, 1986, (Contributed).

35. A. P. Marchand and A.-H. Wu, "Synthesis of New Substituted Pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,0}$]undecanes. A Novel Synthesis of 1,3-Bishomo-pentaprismane", 191st National Meeting of the American Chemical Society, New York, NY, April 15, 1986, (Contributed).

36. A. P. Marchand, "Stereochemistry and Mechanism of the Iron Carbonyl-Promoted Coupling of 7-Substituted Norbornadienes to Carbon Monoxide, Department of Chemistry, University of New Hampshire, Durham, NH, April 17, 1986, (Invited).

37. A. P. Marchand, "Synthesis of New High Energy/High Density Solid and Liquid Polycyclic Hydrocarbon Fuels for Airbreathing Missiles", Navy/Air Force High Energy Hydrocarbon Fuels Contract Review, University of Akron, Akron, OH, April 23, 1986, (Invited).

38. A. P. Marchand and I-hsiung Wang, "Synthesis of 4,6-Dinitropentacyclo-[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane", American Chemical Society Meeting-

in-Miniature, East Texas State University, Commerce, TX, April 25, 1986, (Contributed).

39. A. P. Marchand and An-hsiang Wu, "Syntheses of New Substituted Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecanes. A Novel Synthesis of 1,3-Bishomopentaprismane", American Chemical Society Meeting-in-Miniature, East Texas State University, Commerce, TX, April 25, 1986, (Contributed).

40. W. B. Smith, A. P. Marchand, S. C. Suri, and Pei-wen Jin, "Synthesis of the Two Epimeric 6-Carbomethoxy-1,5-dimethyl-endo-tricyclo-[5.2.1.$0^{2,6}$]dec-8-en-3-ones. Unequivocal Structural Assignment of the 5-Alpha- and 5-Beta-Isomers via 2-D NMR Spectroscopy", American Chemical Society Meeting-in-Miniature, East Texas State University, Commerce, TX, April 25, 1986, (Contributed).

41. A. P. Marchand, G. V. Madhava Sharma, P. R. Pednekar, G. S. Annapurna and T.-C. Chou, "Synthesis of Novel Polycyclic Cage Molecules. Precursors to Potential New High Energy Density Explosives." Fifth Annual Working Group Meeting on Synthesis of High Energy Density Materials, U. S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, Dover, NJ, May 21, 1986, (Invited).

42. A. P. Marchand, "Novel Functionalizations of Pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane", 21st Reaction Mechanisms Conference Department of Chemistry, The University of Texas, Austin, TX, June 22-26, 1986, (Poster Session: Contributed).

43. A. P. Marchand, G. V. Madhava Sharma, P. R. Pednekar, G. S. Annapurna and T.-C. Chou, "Synthesis of Pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]-undecane-4,7,11-trione (D_3-trishomocubanetrione) and Pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-4,8,11-trione", 192nd National Meeting of the American Chemical Society, Anaheim, CA, September 7-12, 1986, Paper No. ORGN-103.

44. A. P. Marchand, "Applications of Mass Spectrometry to Organic

Structural Analysis", Department of Physical Sciences, Bishop College, Dallas, TX, October 20, 1986. (Invited).

45. A. P. Marchand, "Synthesis of New High Energy/High Density Monomers and Polymers: Synthesis of D_3-Hexanitrotrishomocubane". Crystalline Energetic Materials Synthesis Workshop, Office of Naval Research, Chestertown, MD, November 3, 1986, (Invited).

46. A. P. Marchand and P. R. Dave, "Synthesis of 7-Phenoxynorbornadiene and its Thermal Reaction with Iron Pentacarbonyl", 1986 Southwest Regional Meeting of the American Chemical Society, Houston, TX, November 19, 1986, Paper No. 389, (Contributed).

47. A. P. Marchand, G. V. Madhava Sharma, P. R. Pednekar, G. S. Annapurna, and T.-C. Chou, "Syntheses of Pentacyclo[$6.3.0.0^{2,6}.0^{3,10}.0^{5,9}$]-undecane-4,7,11-trione (D_3-Trishomocubanetrione) and Pentacyclo-[$5.4.0.0^{2,6}.0^{3,10}.0^{5,9}$]undecane-4,8,11-trione", 1986 Southwest Regional Meeting of the American Chemical Society, Houston, TX, November 19, 1986, Paper No. 391, (Contributed).

48. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, University of Houston, Houston, TX, November 21, 1986, (Invited).

49. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, University of New Orleans, New Orleans, LA, February 6, 1987, (Invited).

50. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, University of Southern Mississippi, Hattiesburg, MS, February 16, 1987, (Invited).

51. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, McMaster University, Hamilton, Ontario, Canada, March 24, 1987, (Invited).

52. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, York University, Downsview, Ontario, Canada, March 25, 1987, (Invited).

53. A. P. Marchand, "Orbital Symmetry: A Problem-Solving Approach", Department of Chemistry, York University, Downsview, Ontario, Canada, March 25, 1987, (Invited).

54. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, March 26, 1987, (Invited).

55. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, University of Toronto, Toronto, Ontario, Canada, March 27, 1987, (Invited).

56. A. P. Marchand, P. R. Dave, W. H. Watson, Jr., and I Tavanaiepour, "Stereochemistry of the Reaction of 7-Substituted Norbornadienes with Iron Carobnyls. Reaction of $Fe(CO)_5$ with 7-Phenoxy- and 7-(p-cyanophenoxy)-norbornadiene", 193rd National Meeting of the American Chemical Society, Denver, CO, April 8, 1987, Paper No. ORGN-193, (Contributed).

57. A. P. Marchand, "Synthesis of Natural and Unnatural Products", The J. Clarence Karcher Lecture Series, The University of Oklahoma, Norman, OK, April 16, 1987, (Invited).

58. A. P. Marchand, V. Vidyasagar, M. B. Buckner and P. O. Holman, "Lewis Acid Catalysis of a Diels-Alder Cycloaddition. An Undergraduate Organic Experiment", 20th ACS Meeting-in-Miniature, Texas Wesleyan College, Ft. Worth, Texas, April 24, 1987, (Contributed).

59. A. P. Marchand, "Interpretation of Carbon-13 NMR Spectra", Department of Chemistry, University of Dallas, Dallas, TX, April 28, 1987 (Invited).

60. A. P. Marchand, "Synthesis of New Polynitropolycyclic Systems", Department of Chemistry, United States Military Academy, West Point, New York, May 19, 1987, (Invited).

61. A. P. Marchand, "Synthesiss of New Polynitropolycyclic Systems", 6th Working Group Meeting on Synthesis of High Density Energetic Materials, Concord Hotel, Kiamesha Lake, NY, May 21, 1987, (Invited).

62. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, Ching Hua University, Hsinchu, Taiwan, Republic of China, May 26, 1987, (Invited).

63. A. P. Marchand, "Stereochemistry and Mechanism of the Iron Carbonyl-Promoted Coupling of Strained Alkenes to Carbon Monoxide", Institute of Chemistry, Academic Sinica, Nankang, Taipei, Taiwan, Republic of China, May 27, 1987, (Invited).

64. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry Tunghai University, Taichung, Taiwan, Republic of China, May 29, 1987, (Invited).

65. A. P. Marchand, "Synthesis of Novel Cage Molecules and Related Unnatural Products", Department of Applied Chemistry, East China University of Chemical Technology, Shanghai, The People's Republic of China, June 3, 1987, (Invited).

66. A. P. Marchand, "Approaches to the Synthesis of Polyquinane Natural Products", Department of Applied Chemistry, East China University of Chemical Technology, Shanghai, The People's Republic of China, June 4, 1987, (Invited).

67. A. P. Marchand, "Stereochemistry and Mechanism of the Iron Carbonyl-Promoted Coupling of Strained Alkenes to Carbon Monoxide", Department of Applied Chemistry, East China University of Chemical Technology, Shanghai, The People's Republic of China, June 5, 1987, (Invited).

68. A. P. Marchand, "Application of the Principles of Conservation of Orbital Symmetry to Problems in Organic Chemistry", Department of Applied Chemistry, East China University of Chemical Technology, Shanghai, The People's Republic of China, June 8, 1987, (Invited).

69. A. P. Marchand, "Stereochemistry and Mechanism of the Iron Carbonyl-Promoted Coupling of Strained Alkenes to Carbon Monoxide", Department of Applied Chemistry, Shanghai Jiao Tong University, Shanghai, The People's Republic of China, June 9, 1987, (Invited).

70. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, The People's Republic of China, June 10, 1987, (Invited).

71. A. P. Marchand, "Synthesis of Novel Polymers from Polycyclic Cage Monomers", Department of Applied Chemistry, East China University of Chemical Technology, Shanghai, The People's Republic of China, June 11, 1987, (Invited).

72. A. P. Marchand, "Synthesis of Natural and Unnatural Products", Department of Chemistry, Fudan University, Shanghai, The People's Republic of China, June 11, 1987, (Invited).

73. A. P. Marchand, "(a) Stereochemistry and Mechanism of the Ethyl Diazoacetate-Promoted Beta-Elimination of Hydrogen Bromide from Simple Alkyl Halides; (b) Mechanism of Formation of Sulfonium Tetrafluoroborates via Reactions of Gamma, Delta-Unsaturated Ketones with Thiols in the Presence of Boron Trifluoride Etherate", Department of Applied Chemistry, East China University of Chemical Technology, Shanghai, The People's Republic of China, June 12, 1987, (Invited).

74. A. P. Marchand, "Synthesis of Natural and Unnatural Products", School of Pharmacy, West China University of Medical Sciences, Chengdu, The People's Republic of China, June 16, 1987, (Invited).

75. A. P. Marchand, "Stereochemistry and Mechanism of the Iron Carbonyl-Promoted Coupling of Strained Alkenes to Carbon Monoxide", School of Pharmacy, West China University of Medical Sciences, Chengdu, The People's Republic of China, June 16, 1987, (Invited).

76. A. P. Marchand, "(a) Synthesis of Novel Polymers from Polycyclic Cage Monomers; (b) Mechanism of Formation of Sulfonium Tetrafluoroborates via Reactions of Gamma, Delta-Unsaturated Ketones with Thiols in the Presence of Boron Trifluoride Etherate; (c) Reactions of Dichloroketene with Substituted Pentacycloundecanes", School of Pharmacy, West China University of Medical Sciences, Chengdu, The People's Republic of China, June 17,

1987, (Invited).

77. A. P. Marchand, "Stereochemistry and Mechanism of the Iron Carbonyl-Promoted Coupling of Strained Alkenes to Carbon Monoxide", Department of Chemistry, Kyungpook National University, Taegu, South Korea, June 22, 1987, (Invited: Plaque of Appreciation presented by Professor Hak-ki Lee, Head of the Kyungpook District, Korean Chemical Society).

78. A. P. Marchand, G. S. Annapurna, V. Vidyasagar, J. L. Flippen-Anderson, R. Gilardi, C. George and J. L. Ammon, "Synthesis of Nitro-Substituted 2,3,4,8-Tetraphenylpentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]-decanes", 194th National Meeting of the American Chemical Society, New Orleans, LA, August 30-September 4, 1987, Paper No. ORGN-008, (Contributed-Poster Session).

79. A. P. Marchand and G. S. Annapurna, "Pentacyclo-[5.5.0.$0^{4,11}$.$0^{5,9}$.$0^{8,12}$]dodecane-9,12-dione", 194th National Meeting of the American Chemical Society, New Orleans, LA, August 30-September 4, 1987, Paper No. ORGN-009, (Contributed-Poster Session).

80. A. P. Marchand, P. R. Dave and B. E. Arney, Jr., "Studies Directed Toward the Synthesis of 8,8,11,11-Tetranitropentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane", 194th National Meeting of the American Chemical Society, New Orleans, LA, August 30-September 4, 1987, Paper No. ORGN-010, (Contributed-Poster Session).

81. A. P. Marchand, P.-W. Jin, J. L. Flippen-Anderson, R. Gilardi and C. George, "Novel Rearrangement in the 1,3-Bishomocubyl Ring System", 194th National Meeting of the American Chemical Society, New Orleans, LA, August 30-September 4, 1987, Paper No. ORGN-093, (Contributed).

82. A. P. Marchand, B. E. Arney, Jr., R. Gilardi and J. L. Flippen-Anderson, "Lewis Acid-Promoted Reaction of Pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione with Ethyl Diazoacetate", 194th National Meeting of the American Chemical Society, New Orleans, LA, August 30-September 4, 1987, Paper No. ORGN-094, (Contributed).

83. A. P. Marchand, "Synthesis of Natural & Unnatural Products", Department of Chemistry, University of Dallas, Dallas, Texas, September 15, 1987, (Invited).

84. A. P. Marchand, "Synthesis of Natural & Unnatural Products", Department of Chemistry, University of South Florida, Tampa, FL, October 1, 1987, (Invited).

85. A. P. Marchand, "Synthesis of Natural & Unnatural Products", Department of Chemistry, University of Miami, Coral Gables, FL, October 2, 1987, (Invited).

86. A. P. Marchand, "Synthesis of Natural & Unnatural Products", American Cyanamid Company, Lederle Laboratories, Pearl River, NY, October 21, 1987, (Invited).

87. A. P. Marchand, "Synthesis of Natural & Unnatural Products", Department of Chemistry & Chemical Engineering, New Jersey Institute of Technology, Newark, NJ, October 22, 1987, (Invited).

88. A. P. Marchand, B. E. Arney, Jr., G. S. Annapurna, R. Gilardi, and J. L. Flippen-Anderson, "Lewis Acid-Promoted Reaction of Pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione with Ethyl Diazo-acetate", International Symposium on Physical-Organic/Theoretical Chemistry, Austin, Texas, February 25-27, 1988, Poster Session I, February 26, 1988, (Contributed).

89. A. P. Marchand, "Synthesis of New Polynitropolyhedranes", U. S. Air Force High Energy Density Materials Contractors Conference, Newport Beach, CA, February 29-March 2, 1988, (Invited).

90. A. P. Marchand, "Synthesis of Novel, Substituted Polycyclic "Cage" Systems", Lawrence Livermore National Laboratory, Livermore, CA, March 1, 1988, (Invited).